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DESORPTION IN VACUUM

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DESORPTION IN VACUUM

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A general survey is given of our present knowledge in this field. Important discrepancies between the experimental results and the theoretical explanations put forward by the different authors are pointed out. The complexity of the phenomenon is emphasized and the relative importance of the different elementary process is discussed. A limited choice of research is proposed for desorption in vacuum. Theoretical calculation based on simplified models is compared with some experimental results. It is stipulated that the true surface area must be known; a simple experimental method for measuring this surface is described. The experimental curves of desorption are discussed taking account of preliminary results of true surface area measurements. In unbaked systems the absorbed gas layers at the surface are proved to yield the most important part of the total desorption rate. The residual desorption of baked systems in ultrahigh vacuum techniques seems more likely to be a bulk (diffusion, permeation) rather than a surface phenomenon. Analysis by mass spectrometers such as the omegatron is recommended.



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** Numbers in the margin indicate pagination in the original foreign text.

INTRODUCTION

The kinetic theory of gases places a theoretical limit on the maximum pump delivery that can be realized for a given enclosure. To obtain a vacuum as low as 10^{-7} torr, it is necessary to reduce the desorption rate of the materials used. Baking, which is the classical process in tube making, is a highly effective method but often difficult to apply in large and highly complex units. Therefore, it is of importance to be thoroughly familiar with the mechanism of vacuum desorption or, more generally, with the interactions between gas and solid along their interfaces at low pressure, if a more rational means of control is to be discovered.

This particular report has the purpose of making a qualitative and quantitative analysis of the experimental data on desorption at ambient temperature, which data are beginning to be available in a relatively large volume. For this, we start from some rather simple hypotheses on the elementary mechanisms and the binding energies of adsorbate-adsorbent. The total amount of desorbed gas, experimentally determined and calculated, is such that a revision of the concept of "surface" becomes necessary. We will describe some surface models, give several preliminary results on specific surface, and indicate research trends. Next to knowing the geometry of the surface, its physical characteristics are of importance for understanding the nature and magnitude of the binding forces between solid and adsorbed gases; this constitutes still another research direction. The importance of diffusion and permeation will be discussed. In addition, the necessity of developing high-precision methods for measuring and analyzing extremely low desorption rates will be explained.

1. Measuring the Desorption Rate

A number of vacuum specialists have measured the desorption rate of various materials used in vacuum technology; we cite particularly Dayton (Bibl.1, 2, 3), Blears (Bibl.4), Jaeckel and Schittko (Bibl.5), Santeler (Bibl.6), Power and Crawley (Bibl.7), Henry (Bibl.8), Geller (Bibl.9), and Boulassier (Bibl.10). Recently, Dayton (Bibl.3) made a survey of the present knowledge within this field. He proposed a theoretical interpretation of the test results, with special emphasis on the diffusion of gas in the solid toward the vacuum end. Krauss (Bibl.11) believed that principally a surface phenomenon ¹⁵⁶ is involved here. The experimental curves of the desorption rate, plotted as a function of the pumping time, frequently show widely differing slopes for one and the same material. In general, straight lines in log-log presentation are involved, with slopes varying between -0.5 and -2. It is well possible that the experimental techniques and the preparation of the specimens (as well as the composition and constitution of the material) are responsible for some of the deviations. We conducted several experiments, using the conventional method of pumping from the vessel containing the specimen across a weak conductance of known value; however, we made continuous comparisons with an identical evacuated vessel, thus eliminating the influence of desorption of the vessel to the greatest possible extent. Figure 1 shows the experimental device.

All joints are of metal and a freeze trap eliminates the influence of oil vapors.

The desorption per cm^2 of the specimen is equal to

$$q = \frac{C}{A} (p_1 - p_2)$$

where

q = desorption rate, in $\text{l} \cdot \text{torr}/\text{sec} \cdot \text{cm}^2$ (or in $\text{particles}/\text{sec} \cdot \text{cm}^2$)

C = conductance of the orifice, in l/sec (or in $\text{particles}/\text{sec}$)

A = surface of the specimen, in cm^2 .

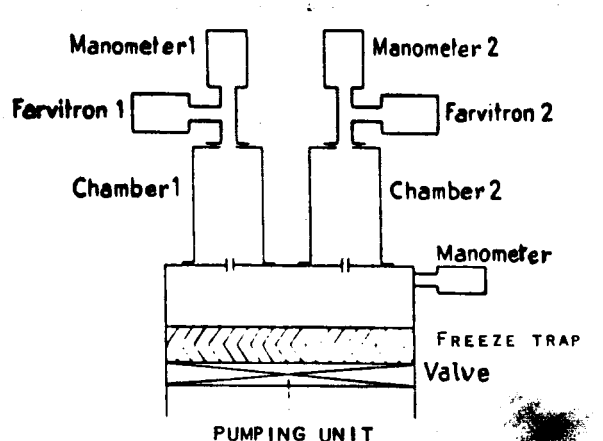


Fig.1 Measuring the Desorption Rate

$$q = \frac{C}{A} (p_1 - p_2) \quad p = Ki$$

$$\frac{dq}{q} = \frac{\frac{\Delta K}{K}}{\frac{\Delta i}{i}} \quad \Delta i = \frac{1}{K} (p_1 - p_2)$$

The measurements are excellently reproducible. A systematic error, due to the difference in desorption from the two vacuum bell jars, is equal to

$$\frac{dq}{q} = \frac{\Delta K/K}{\Delta i/i}$$

where ΔK denotes a difference of the manometer constants equivalent to the difference of the desorption curves $q = f(t)$ of the two vacuum jars:

and
$$\Delta i = \frac{1}{K} (p_1 - p_2)$$

$$i = p_1/K$$

This error does not influence the slope of the curves; the conductance of the orifice is of the order of 1 l/sec and the surface of the specimens of the order of 10^3 cm^2 . The specimens are degreased with trichloroethylene and cleaned with ethyl alcohol. Figures 2 and 3 show several curves for metals and nonmetals.

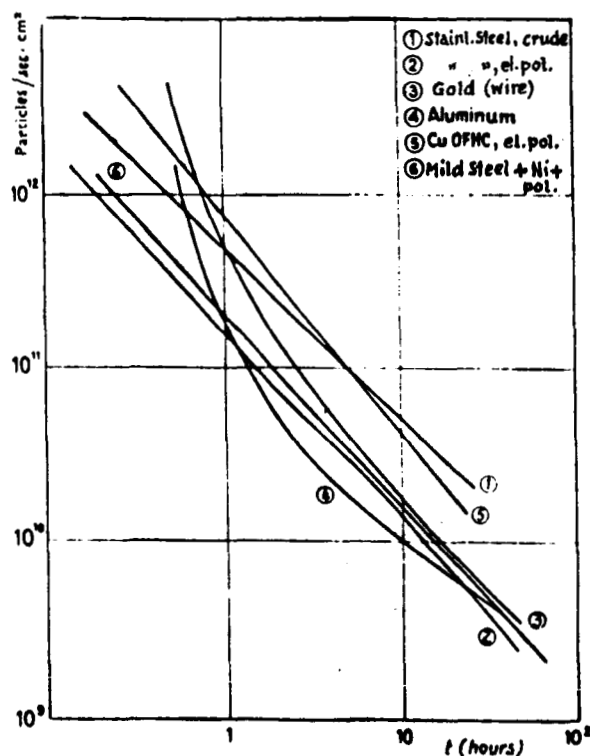


Fig.2

Figures 4, 5, and 6 give the desorption rates and the slopes of the $q = 157 = f(t)$ curves after 1 hr, 10 hrs, 25 hrs, and 50 hrs of pumping, for different materials.

After 10-hr pumping, the slope is still between -0.4 and -2 and, specifically, the metals remain in the vicinity of -1 and, rarely, near -0.75.

2. Various Elementary Mechanisms

Desorption in vacuum is a highly complex phenomenon. The elementary mech-

anisms to be considered are the following:

Adsorption

Adsorption can be either physical (we are thinking specifically of capillary condensation) or chemical. In the former case, the energies involved are

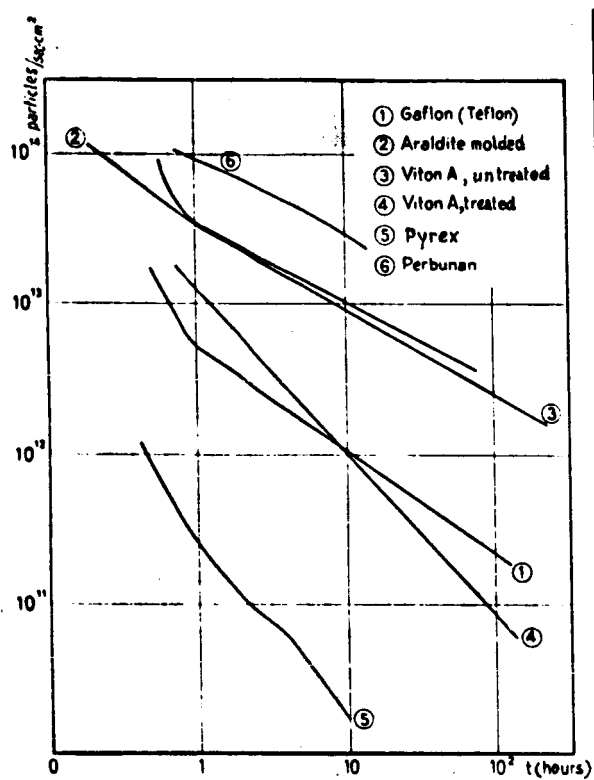


Fig.3

extremely low and we agree with Dayton that they can be neglected since, theoretically, a few minutes of pumping are sufficient to eliminate any trace of physical adsorption of the usual gases. Chemical adsorption can be activated (slow adsorption) or nonactivated (rapid adsorption) and can take place after a preliminary dissociation of the molecule or else directly. Chemisorption never extends farther than one monomolecular layer.

Absorption

Adsorbed particles are able to go in solution within the solid by diffusion. For this, an activation energy is necessary, i.e., a slow phenomenon at ambient temperature is involved.

Surface Desorption

This phenomenon is the opposite of adsorption and requires an activation energy equal to the sum of the binding energy and the activation energy of adsorption. The binding energy is not necessarily constant over the entire surface, either because of heterogeneity of the surfaces or, which is more probable, because of interaction between the adsorbed particles.

Diffusion

At the interior of the solid, the gas may diffuse toward the surface because of the concentration gradient and because of having acquired the necessary activation energy. Here, a diffusion through the crystals constituting the solid or else a diffusion along the grains in the fissures and pores may be involved. The concentrations and, specifically, the activation energies will differ widely.

Permeation

Gas is able to permeate the walls of a vacuum enclosure by adsorption on the external surface, followed by diffusion, generally after preliminary dissociation.

Material	Treatment	1 hour		10 hours		25 hours		50 hours	
		$10^{10} \text{ s}^{-1} \text{ cm}^{-2}$	slope	$10^{10} \text{ s}^{-1} \text{ cm}^{-2}$	slope	$10^{10} \text{ s}^{-1} \text{ cm}^{-2}$	slope	$10^{10} \text{ s}^{-1} \text{ cm}^{-2}$	slope
Gold	Crude wire	515	2.1	1.8	1	0.68	1	0.34	0.9
Mild steel	pickled	1012	0.6	960	0.7				
Aluminum	virgin	20.5	1	1.95	1	0.76	1	0.28	1
Aluminum	degassed 24 h	13.5	3.2	1	0.9	0.54	0.9	0.22	0.9
Aluminum	3 hrs in air	21.3	1.9	1.55	0.9	0.68	0.9	0.35	0.9
Aluminum	Crude	20.2	1	1.09	0.9	0.86	0.9	0.5	0.9
Aluminum	oxid. Anod. pores 2 μ	900	0.9	105	0.9				
Aluminum	oxid. Anod. pores 5 μ	90	0.1	16	3				
Aluminum	oxid. Anod. th. 2 μ r # 2 μ	110	2.5	3.3	1				
Aluminum	ox. Anod. th. 2 μ , r # 2 μ 3x in air	100	0.9	7.5	2.7				
Aluminum	ox. Anod. th. 20 μ r # 2 μ	1950	1	115	1				
Aluminum	ox. Anod. th. 20 μ r # 2 μ 1 mo in air	800	1.3	60	1.3				
Aluminum	ox. Anod. th. 100 μ at 30 V, r # 2 μ	4000	1.3	320	1.3				
Aluminum	ox. Anod. th. 100 μ at 30 V r # 2 μ , 1 mo in air	6000	1.4	390	1.4				
Aluminum	ox. Anod. th. 100 μ at 50 V r > 2 μ	4800	1.3	370	1.3	130	1.3		
Aluminum	ox. Anod. th. 100 μ at 50 V r > 2 μ 1 mo in air	7500	1.7	400	1.7				
Copper	Mech. polished	11.4	1	1.16	1	0.47	1	0.23	1
Cu - OFHC	Crude	61.2	1.3	4.1	1.3	1.35	1.3		
Cu - OFHC	Mech. polished	6.2	1.1	0.53	1.1	0.2	1.1	0.12	0.4
Cu	Crude	130	1	13.5	1	5.7	1	1.8	1

Fig.4 Experimental Desorption Constants

MATERIAL	TREATMENT	1 hour		10 hours		25 hours		50 hours	
		$10^{10} \text{ s}^{-1} \text{ cm}^{-2}$	slope	$10^{10} \text{ s}^{-1} \text{ cm}^{-2}$	slope	$10^{10} \text{ s}^{-1} \text{ cm}^{-2}$	slope	$10^{10} \text{ s}^{-1} \text{ cm}^{-2}$	slope
Mild steel	Chrom., electro, crude	23	1	1.9	1	0.8	1	0.4	1
Mild steel	Chrom., electro, pol	29.7	1	2.6	1	1	1	0.48	1
Mild steel	Ni, electro, crude	13.8	0.9	1.38	0.9	0.57	0.9		
Mild steel	Ni, electro-pol.	9	1.1	0.76	1.1	0.3	1.1		
Mild steel	Ni, chem., crude	27	1	2.3	1	0.9	1	0.42	1
Mild steel	Ni, chemical, pol.	17	1	1.5	1	0.6	1	0.28	1
Stainless	ICN 472 crude	44	0.9	4.8	0.9	2	0.9		
Stainless	ICN 472 sand-cast	27	1.2	3.4	0.8				
Stainless	NS22S pol. mech.	5.6	0.5	1.5	0.7	0.72	0.7	0.43	0.7
Stainless	NS22S pol. electr.	14	1	1.4	1	0.5	1.22	0.2	1.2
Stainless	NS22S crude	47	1.3	4.4	1.9	1.1	2.4		
Molybd.	crude	17	1	1.2	1	0.5	0.9	0.3	0.9
Sulfur-Zn	crude	720	1.4	105	0.8	63	0.3	51	0.05
Ti	crude	37	0.6	6	1.1	1.7	0.2		
Ti	crude	13	1	1.2	1	0.4	1	0.2	1

Fig.5 Experimental Desorption Constants

3. Kinetics of the Elementary Mechanisms

Chemical Adsorption

In the terminology of Trapnell (Bibl.12), the chemical adsorption is expressed by

$$\frac{dn}{dt} = \sigma \vartheta(p) f(\theta) e^{\frac{E_a}{RT}} (1) \quad \vartheta(p) = \frac{p}{\sqrt{2\pi m k T}} \quad \left| \begin{array}{l} \theta = \frac{n}{n_s} \\ \sigma \rightarrow 1 \end{array} \right.$$

without dissociation: $f(\theta) = 1 - \theta$ |

with dissociation:

(or one molecule adsorbed on two sites)

$$\begin{array}{l} f(\theta) = \frac{z}{z-\theta} (1-\theta)^2 \quad \text{stationary layers} \\ \text{with } \frac{\theta}{1-\theta} = \frac{\varepsilon(1+\eta\varepsilon)}{1+\varepsilon} \quad \left\{ \begin{array}{l} \text{moving} \\ \text{layers} \end{array} \right. \\ f(\theta) = \frac{1-\theta}{1+\varepsilon} \quad \eta = e^{-V/RT} \\ \text{for } \theta \rightarrow 0 \quad \text{we have} \end{array}$$

Here, V is the interaction energy between adjacent particles, while Z denotes 59 the number of directly adjacent sites. The probability of adsorption (sticking probability) is defined as

$$s = \sigma f(\theta) e^{\frac{E_a}{RT}} \quad \left| \right.$$

It was found that s is constant for θ between 0 and about 0.3. Probably, a physical adsorption on already chemisorbed particles is involved here, followed by a superficial diffusion toward sites free for chemisorption. Consequently, for $0 < \theta < 0.3$, the above expressions $f(\theta)$ are not always valid.

When the pressure of the ambient gas is very low and when the surface is already extensively coated, $f(\theta)$ and $\vartheta(p)$ will also have very low values so

that, specifically if the adsorption is preceded by a dissociation, $\frac{dn}{dt}$ becomes negligible.

Chemical Desorption

In general, E is not constant but is a function of θ (or of n). Specifically, we will study here the case of $E = E_0 - \alpha\theta$, which will lead to the Temkin

MATERIAL	TREATMENT	1 hour		10 hours		25 hours		50 hours	
		$10^{10} s^{-1} cm^{-2}$	slope	$10^{10} s^{-1} cm^{-2}$	slope	$10^{10} s^{-1} cm^{-2}$	slope	$10^{10} s^{-1} cm^{-2}$	slope
Gaffon	Crude	543	0.8	108	0.9	57	0.9	37	0.9
Perbunan	Crude	10 000	0.15	3 000	0.6				
Molybd. glass	Crude tube	21	1.1	1.3	1.1				
Pyrex glass	Crude	24	1.1	1.8	1.7				
Pyrex glass	1 mo. in air str.	3.8	0.9	0.53	0.7				
Araldite	Molded	3 800	0.8	1 150	0.8	700	0.8	490	0.8
Terephenyl	Crude	2 030	0.5	550	0.5	330	0.5	204	0.5
Viton A	Crude	3 720	0.8	1 000	0.4	604	0.4	400	0.4
Viton A	at 170 °C 3 hrs in vac.	1 296	1	100	1.3	40	1.4	19	1.5

Fig.6 Experimental Desorption Constants

isotherm if it is assumed that

$$\left(\frac{dn}{dt}\right)_{ads} + \left(\frac{dn}{dt}\right)_{des} = 0$$

$$\text{i.e.: } \frac{\alpha \theta}{j \log \left(\frac{1}{\theta} - 1\right)} = \log C_p$$

where $j = 2$ or 1 , depending on whether there is a dissociation or not.

We will discuss here the physical reasons for this linear dependence of E on θ . It may well be possible that heterogeneity of the surface, interaction between particles, or gas mixtures at different E_0 are involved; however, this is of no importance for the reasons given below.

$$\frac{dn}{dt} = -Kf'(0) e^{\frac{E}{RT}} \text{ or } \frac{dn}{dt} = -A f(n) e^{\frac{E}{RT}} \quad (2)$$

If, for adsorption, the constant σ actually is a constant independent of n , the value of K (or of A) is even more disputable. In the following, we assume K to be constant.

If the particles are adsorbed without previous dissociation, we have

$$f'(0) = \theta.$$

In the opposite case, we have $f'(0) = 0^2$.

In the case of physisorption or chemisorption without dissociation, the Polanyi-Wigner equation will permit an interesting identification of K :

$$\frac{dn}{dt} = -\partial n_s \theta e^{\frac{E}{RT}} \quad (3)$$

and thus $K = \partial n_s$.

Here, ∂ has the dimension of the inverse of a time of the order of the vibration period of the particles, vertically to the surface

$$\frac{dn}{dt} = -\frac{n_s \theta}{\tau} \text{ with } \tau = \tau_0 e^{\frac{E}{RT}}$$

$$\partial = \frac{1}{\tau_0} \quad K = \frac{n_s}{\tau_0}$$

This represents the sticking time τ .

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Above, τ_0 is of the order of 10^{-13} sec so that, in this case, we can attribute a value of 10^{28} particles/sec \cdot cm² to K . Assuming that one monomolecular layer is composed of 10^{15} particles/cm², by using known values of the physisorption for E (up to about 10 kcal/mole), it seems that the sticking time is extremely short and, consequently, the desorption is extremely rapid.

5. Remarks

In the remainder of our discussion, $\frac{dn}{dt}$ will denote the variation in the number of particles per true unit surface, i.e., the experimentally measured rate of desorption, which we will also denote by q if the true surface is equal to the apparent geometric surface. Consequently, their value will be negative.

Diffusion

The two Fick laws permit calculating the gas flux diffusing per sec/cm² of surface:

$$\left. \begin{aligned} q &= -D \frac{\partial C}{\partial x} & D &= D_0 e^{-\frac{Q}{RT}} \\ \frac{\partial C}{\partial t} &= D \frac{\partial^2 C}{\partial x^2} \end{aligned} \right| \quad (4)$$

where C denotes the concentration, D the diffusion constant, and Q the activation energy.

Depending on the boundary conditions, different solutions will be obtained.

1 - Assuming a semi-infinite solid:

$$\left. \begin{aligned} C(0, x) &= C_0 \\ q &= -D \left(\frac{\partial C}{\partial x} \right)_{x=0} \end{aligned} \right|$$

the solution will be

$$C(x, t) = \frac{C_0}{2} \left[1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right] \quad (5)$$

from which it follows that the amount of gas transferred by diffusion to the solid-gas interface for $x = 0$, per unit surface and unit time, will be

$$\left. \begin{aligned} q &= -\frac{C_0}{2} \sqrt{\frac{D}{\pi}} \cdot \frac{1}{\sqrt{t}} \\ \log(-q) &= \log \left[\frac{C_0}{2} \sqrt{\frac{D}{\pi}} \right] - \frac{1}{2} \log t \end{aligned} \right| \quad (6)$$

2 - Assuming that the solid is limited by two parallel planes (layers of a thickness l)

$$C(0, x) = C_0$$

$$q = -D \left(\frac{\partial C}{\partial x} \right)_{x=0}$$

the solution will be

$$C = \frac{4 C_0}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \frac{(2n+1)\pi x}{2} \exp \left[-\frac{D(2n+1)^2 \pi^2 t}{l^2} \right] \quad (7)$$

and $q = \frac{4 C_0 D}{l} \exp \left[-\frac{D \pi^2 t}{l^2} \right]$ if the calculation is limited to the first term of the sum.

It is easy to demonstrate that this latter solution for q can also be written under the form of the first solution (linear law with the slope $-1/2$ in log-log coordinates) if l becomes greater than $\sqrt{\pi D t}$. This condition (for hydrogen, D is of the order of 10^{-8} to 10^{-10} cm^2/sec in conventional metals and even much lower for the other gases) will almost always be satisfied for normal values of D and for times that are not too short. Then, it can be stated that from $l = 0.01$ cm, the solution for the semi-infinite solid will remain valid. At the beginning of desorption, a thin layer underneath the surface, specifically if the concentration there is high and the diffusion coefficient relatively large, may lead to a diffusion with an exponential decrease in q .

Permeation

Permeation is defined as

$$P = -D \frac{\partial C}{\partial x}$$

in the stationary regime where $\frac{\partial C}{\partial x}$ is the concentration gradient which is

assumed as constant between the two surfaces. Because of the exponential dependence of D on the temperature, we can write

$$P = P_0 e^{-\frac{Q}{RT}}$$

Practically, the same activation energy that prevails in diffusion is involved here. In fact, permeation is a much more complex phenomenon since the surface phenomena such as adsorption, dissociation, and absorption may play a pre- /61 dominant role. The solubility of the gas, as a function of the temperature (generally, a function increasing with the temperature), led Richardson to derive the following formula:

$$P = \frac{k}{l} \sqrt{pT} e^{-\frac{b}{T}}$$

where l denotes the thickness of the wall, k is a constant, p is the pressure (in the general case in which the molecules are first dissociated before being absorbed), and b is an activation energy.

It is thus obvious that the state of the external surface, where the gas enters, will frequently be determining for the permeation.

Expressions for $q = f(t)$

We will derive below expressions $q = \frac{dn}{dt} = f(t)$ for various cases that may be encountered.

The basic hypotheses are extremely simple:

K (or A) in the expression for the superficial desorption is constant.

Only one gas is involved.

The temperature is constant (ambient temperature).

No hypothesis will be made as yet on the concept of surface.

First Case: Negligible adsorption above ambient pressure (p practically equal to zero).

1.1 Without Dissociation

For example the case of CO.

1.1.1 $E = E_0$ constant

$$\frac{dn}{dt} = -A n e^{-\frac{E_0}{RT}} \quad (8)$$

Integration is direct

or

$$\begin{aligned} \log \left(-\frac{dn}{dt} \right) &= \log \left(-\frac{dn}{dt} \right)_{t_0} - A e^{-\frac{E_0}{RT}} (t - t_0) \\ \log (-q) &= \log (-q_0) + \frac{1}{n_s} q_0 (t - t_0) \end{aligned} \quad (9)$$

Consequently, $q = f(t)$ is a straight line in semilogarithmic coordinates with a slope $\frac{1}{n_s} q_0$ where n_s is the saturation concentration per cm^2 of surface.

1.1.2 $E = E_0 - \alpha \frac{n}{n_s}$ (Temkin isotherm)

$$\frac{dn}{dt} = -A n e^{-\left(E_0 - \alpha \frac{n}{n_s}\right) \cdot \frac{1}{RT}} \quad (10)$$

Deriving with respect to t and eliminating A , we obtain

$$\frac{d^2 n}{dt^2} - \left(\frac{1}{n} + \beta \right) \left(\frac{dn}{dt} \right)^2 = 0 \text{ at } \beta = \frac{\alpha}{n_s RT} \quad (11)$$

After finding simple solutions for this differential equation, two extreme cases can be considered:

1.1.2.1 $\frac{1}{n} \ll \beta$

i.e., n is very large, of the order of magnitude of n_s , or (and) α is large, of the order of magnitude of 10 kcal/mole or more (this reduces to considering n

constant in the nonexponential term).

The solution then becomes very simple

$$\frac{dn}{dt} = - \frac{\left(\frac{dn}{dt}\right)_0}{\beta \left(\frac{dn}{dt}\right)_0 (t - t_0) - 1}$$

or $q = \frac{q_0}{1 - \beta q_0 (t - t_0)}$

(12)

(it should be noted here that q and q_0 are negative).

Since βq_0 here is roughly of the order of 1, we can simplify for $t > 100$ sec:

$$q = - \frac{1}{\beta (t - t_0)}$$

$$\log(-q) = - \log \beta - \log(t - t_0)$$
(13)

In this case, $q = f(t)$ is a straight line in log-log coordinates with a slope of -1. Frequently, the metal surfaces obey this law of desorption, even up to 100 hrs of pumping. Below, we will demonstrate that then the condition $\frac{1}{n} \ll \beta$ must be taken into consideration:

1.1.2.2 $\frac{1}{n} \gg \beta$

(12)

This applies if n is small, or α is small, or n and α are small.

The differential equation is the same as that given for $E = E_0$, i.e.,

$$\log(-q) : \log(-q_0) + \frac{1}{n_0} q_0 (t - t_0)$$
(9)

1.2 With Dissociation

1.2.1 $E = E_0$ constant

$$\frac{dn}{dt} = - A n^2 e^{-\frac{E_0}{RT}}$$
(14)

The integration is direct

$$\frac{dn}{dt} = \left(\frac{dn}{dt}\right)_0 \frac{1}{\left[1 + \left(\frac{dn}{dt}\right)_0 \frac{(t-t_0)}{n_s}\right]^2} \quad (15)$$

or, for a sufficiently large t ,

$$\begin{aligned} \frac{dn}{dt} &= \frac{n_s^2}{\left(\frac{dn}{dt}\right)_0} \cdot \frac{1}{(t-t_0)^2} \\ \log(-q) &= \log\left(-\frac{n_s^2}{q_0}\right) - 2 \log(t-t_0) \end{aligned} \quad (16)$$

i.e., $q = f(t)$, in log-log coordinates, becomes a straight line at a slope of -2.

1.2.2 $E = E_0 - \alpha \frac{n}{n_s}$ (Temkin isotherm)

$$\frac{dn}{dt} = -A n^2 e^{-\left(E_0 - \alpha \frac{n}{n_s}\right) \cdot \frac{1}{RT}} \quad (17)$$

$$\frac{dn^2}{dt^2} - \left(\frac{2}{n} + \beta\right) \left(\frac{dn}{dt}\right)^2 = 0 \text{ at } \beta = \frac{\alpha}{n_s RT} \quad (18)$$

Again, we will differentiate between two extreme cases which yield the same solution as in the case without dissociation.

1.2.2.1

$$\begin{aligned} \frac{2}{n} &\ll \beta \\ \frac{dn}{dt} &= -\frac{\left(\frac{dn}{dt}\right)_0}{\beta \left(\frac{dn}{dt}\right)_0 (t-t_0) - 1} \end{aligned}$$

and, for a sufficiently large t ,

$$\log(-q) = -\log \beta - \log(t-t_0)$$

2.2.2

$$\frac{2}{n} \gg \beta$$

This condition is physically equivalent to a constant energy E, i.e.,

$$\log(-q) = \log\left(-\frac{n_s^2}{q_0}\right) - 2 \log(t - t_0) \quad (16)$$

Second Case: General Case.

The measured desorption is lower than the true desorption in view of the fact that also a re-adsorption occurs above the pressure of the ambient gas in the experimental enclosure.

$$1. E = E_0 \quad |$$

Without Dissociation

$$\frac{dn}{dt} = -A n e^{-\frac{E_0}{RT}} + D e^{-\frac{E_0}{RT}} (n_s - n) p \quad (19)$$

$$\text{By setting } B = A e^{-\frac{E_0}{RT}} \text{ and } C = D e^{-\frac{E_0}{RT}}$$

the following solution is immediately obtained:

$$\begin{aligned} \frac{dn}{dt} &= -n_s (B + Cp) \exp[-(B + Cp)(t - t_0)] \\ \log(-q) &= \log[(B + Cp)n_s] - (B + Cp)(t - t_0) \end{aligned} \quad (20)$$

i.e., a straight line in semilogarithmic coordinates with a slope that increases in absolute value with the pressure. It is obvious that $p = 0$ gives the same solution as eq.(9).

With Dissociation

$$\frac{dn}{dt} = -A n^2 e^{-\frac{E_0}{RT}} + D e^{-\frac{E_0}{RT}} (n_s - n)^2 p \quad (21)$$

which is a difficult differential equation. However, if n differs little /63

from n_s and if p is low, the adsorption term may be more readily neglected than in the case without dissociation.

$$2. \quad E = E_0 - \alpha \frac{n}{n_s}$$

2.1 Without Dissociation

If E_0 is replaced by $E_0 - \alpha \frac{n}{n_s}$ in eq.(19) and if we derive toward t by eliminating A , the following is obtained:

$$\left. \begin{aligned} \frac{d^2 n}{dt^2} - \left(\frac{1}{n} + \beta \right) \left(\frac{dn}{dt} \right)^2 \\ + C_p \left[(n_s - n) \left(\frac{1}{n} + \beta \right) + 1 \right] \frac{dn}{dt} = 0 \end{aligned} \right| \quad (22)$$

Only the extreme case $\frac{1}{n} \ll \beta$ yields a direct integration:

$$\left. \frac{dn}{dt} = \frac{C_p \left(\frac{dn}{dt} \right)_0}{\beta \left(\frac{dn}{dt} \right)_0 - \left[\beta \left(\frac{dn}{dt} \right)_0 - C_p \right] e^{(t-t_0)C_p}} \right| \quad (23)$$

if p is small:

$$\left. \frac{dn}{dt} = \frac{\left(\frac{dn}{dt} \right)_0}{\beta \left(\frac{dn}{dt} \right)_0 - \left[\beta \left(\frac{dn}{dt} \right)_0 - C_p \right] (t - t_0)} \right| \quad (24)$$

For sufficiently long times, we can write

$$\frac{dn}{dt} = - \frac{1}{\left[\beta - C_p \left(\frac{1}{\left(\frac{dn}{dt} \right)_0} \right) \right] (t - t_0)}$$

or

$$\log(-q) = - \log \left[\beta - \frac{C_p}{q_0} \right] - \log(t - t_0) \quad (25)$$

i.e., this again yields a straight line with a slope of -1, in log-log coordinates.

2.2 With Dissociation

The differential equation analogous to eq.(22) then becomes

$$\frac{d^2 n}{dt^2} - \left(\frac{2}{n} + \beta\right) \left(\frac{dn}{dt}\right)^2 + Cp(n_s - n) \left[2 + (n_s - n) \left(\frac{2}{n} + \beta\right)\right] \frac{dn}{dt} = 0 \quad (26)$$

Let us again differentiate two extreme cases:

Physically, this means that we are at the beginning of desorption, i.e., $n_s \sim n$, which goes back to the differential equation without adsorption:

$$\frac{d^2 n}{dt^2} - \beta \left(\frac{dn}{dt}\right)^2 = 0$$

with the same solution as that of eq.(13), i.e., a straight line with a slope of -1, in log-log coordinates.

2.2.2

This corresponds physically to the case $E = E_0$, leading back to the solution of eq.(20) (without dissociation).

6. Total Amount of Desorbed Gas

For the various forms of the functions q , it is possible to find an expression for the total amount desorbed between t_0 and t by simple integration.

The form $q = a e^{-\gamma t}$ yields

$$Q_{t-t_0} = n_s \left[1 - e^{\frac{1}{n_s} q_0 (t-t_0)} \right] \quad (27)$$

The form $q = \frac{b}{t}$ gives

$$Q_{t-t_0} = \frac{n_s RT}{\alpha} \log \left[1 + \frac{q_0 d}{n_s RT} (t-t_0) \right] \quad (28)$$

The form $q = \frac{c}{t^2}$ yields

$$Q_{t-t_0} = n_s \left[1 - \frac{1}{1 - \frac{q_0}{n_s} (t-t_0)} \right] \quad (29)$$

Figures 7 and 8 represent a compilation of the various laws $q = f(t)$ in accordance with the extremely simple hypotheses adopted here.

7. Discussion

Experimentally, metallic surfaces in most cases desorb in accordance with a law approximately in $1/t$. The last Table (Fig.10) indicates that the phenomenon can possibly be described by a Temkin isotherm, i.e., $E = E_0 - \alpha \frac{n}{n_s}$, provided that the concentration of particles adsorbed on the surface does not differ too much from the saturation n_s and that α is relatively large, of the order of 10^4 cal/mole or more. This also holds for molecules that are first dissociated as well as for the other molecules and even for the case that an adsorption takes place, under the condition that the pressure remains very low.

Plastic materials such as araldites, various types of synthetic rubber, etc. generally desorb in accordance with a law near $1/\sqrt{t}$. In that case, diffusion is definitely the predominant phenomenon. Let us mention the specific case of Viton A for which we have plotted a curve in $1/\sqrt{t}$ before thermal treatment in vacuum and a curve in $1/t$ several hours after this treatment: First, we obtained a diffusion of the gas in solution, which was largely elimi-

$\epsilon \ll \frac{u}{2}$

nated by the treatment, followed by surface desorption. It is also of interest that various types of transparent plastics (pyrex and molybdenum glass) desorb

	Without Dissociation	With Dissociation
Without adsorption		
$E = E_0$	$\log(-q) = \log(-q_0) + \frac{1}{n_s} q_0 (t - t_0)$ $Q_{t-t_0} = n_s \left[1 - e^{-\frac{1}{n_s} q_0 (t-t_0)} \right]$	$\log(-q) = \log \left[\frac{-n_s^2}{q_0} \right] - 2 \log(t - t_0)$ $Q_{t-t_0} = n_s \left[1 - \frac{1}{1 - \frac{q_0}{n_s} (t - t_0)} \right]$
$E = E_0 - \alpha \frac{n}{n_s} \quad \frac{1}{n} \ll \beta$ $\frac{1}{n} \gg \beta$	$\log(-q) = -\log \beta - \log(t - t_0)$ $Q_{t-t_0} = n_s \frac{RT}{\alpha} \log \left[1 + \frac{q_0 \alpha}{n_s RT} (t - t_0) \right]$ $\log(-q) = \log(-q_0) + \frac{1}{n_s} q_0 (t - t_0)$ $Q_{t-t_0} = n_s \left[1 - e^{-\frac{1}{n_s} q_0 (t-t_0)} \right]$	$\log(-q) = -\log \beta - \log(t - t_0)$ $\log(-q) = \log \left[\frac{-n_s^2}{q_0} \right] - 2 \log(t - t_0)$ $Q_{t-t_0} = n_s \left[1 - \frac{1}{1 - \frac{q_0}{n_s} (t - t_0)} \right]$
With adsorption $E = E_0$	$\log(-q) = \log [n_s (B + C\rho)] - (B + C\rho) (t - t_0)$ $B = A e^{-E_0/RT}$ $C = D e^{-E_0/RT}$	
$E = E_0 - \alpha \frac{n}{n_s} \quad \frac{1}{n} \ll \beta$ $\frac{1}{n} \gg \beta$	$q = \frac{C p q_0}{\beta q_0 - [\beta q_0 - C p] e^{(t-t_0) C p}}$ $p \rightarrow 0$ $q = \frac{q_0}{1 - [\beta q_0 - C p] (t - t_0)}$	<p>solution without adsorption:</p> $\log(-q) = -\log \beta - \log(t - t_0)$ $E = E_0$

Fig.7 Desorption at Constant K (or A)

in accordance with $1/t$ at ambient temperature, which apparently eliminates /65 the diffusion. Certain curves for metals published by Blears (Bibl.4) show, in log-log coordinates, a slope of the order of (-2) while other curves approach a straight line in semilogarithmic coordinates. According to Fig.10, it seems

that the former may be explained by a desorption of particles dissociated on the surface with a constant binding energy or with a binding energy decreasing

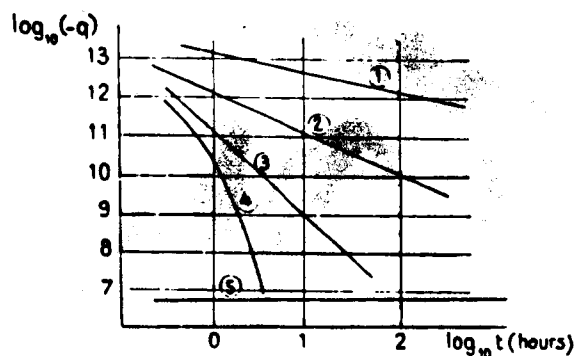


Fig.8 Curves $q = f(t)$

1) $q \sim \frac{1}{t^{1/2}}$ Diffusion.

2) $q \sim \frac{1}{t}$ Without adsorption. $E = E_0 - \alpha \frac{n}{n_s}$ and $\frac{1}{n} \ll \beta$

With or without dissociation.

With adsorption $E = E_0 - \alpha \frac{n}{n_s}$ and $\frac{1}{n} \ll \beta$

With dissociation.

Without dissociation if p is small.

3) $q \sim \frac{1}{t^2}$ Without adsorption. With dissociation $E = E_0$

$E = E_0 - \alpha \frac{n}{n_s}$ and $\frac{1}{n} \gg \beta$

4) $q \sim e^{-\alpha t}$ Without adsorption, without dissociation $E = E_0$

$E = E_0 - \alpha \frac{n}{n_s}$ and $\frac{1}{n} \gg \beta$

With adsorption, without dissociation $E = E_0$

5) $q = q_p$ Permeation in stationary regime.

linearly with the rate of deposition (Temkin) but at a very low concentration and (or) a negligible variation in this energy; the other curves may be ex-

plained by a desorption of undissociated particles under the same conditions.

Although cases exist in which the curves $q = f(t)$ retain a constant slope during a time of about 100 hours, it is obvious that only a part of the total desorption is involved here; specifically the gas flux q_0 , the initial desorption, and the very low final rate of desorption ($10^{-10} \text{ l} \cdot \text{torr/sec} \cdot \text{cm}^2$) are extremely difficult to measure. It is impossible to represent all phenomena of desorption on the basis of a single isotherm. An experimental slope, intermediate between 0.5 and -1 or between -1 and -2, can be explained on the basis of intermediate hypotheses (see Fig.10) and specifically on the value of $\frac{1}{n}$ with respect to $\beta = \frac{\alpha}{n_s RT}$ and the relation between E and θ . In some cases, the slope of the curve shows an inflection toward values lower than -1 after a few tens of hours of pumping: Here, the diffusion starts playing a role.

8. The Surface Problems

On integrating the experimental curves or on calculating the total desorbed quantity according to a formula corresponding to the experimental curve, values will be found which frequently exceed 100 times the quantity furnished by a monomolecular layer of the apparent geometric surface.

It is understandable that, for this reason, surface desorption was not believed to be the principal mechanism and that diffusion was held responsible for the observed desorption rate. However, it seems much more logical - in accordance with our above statements - to assume that surface desorption constitutes the main mechanism and to expand the surface concept. The ratio of the true surface to the apparent geometric surface f , which may be denoted as the specific surface, therefore must be able to exceed 100 or, which comes to the same, n_s must be able to exceed 10^{17} particles per cm^2 of apparent surface.

In this case, at a f of several tens, the hypothesis of the Temkin isotherm ($E = E_0 - \alpha \frac{n}{n_s}$) and an evaluation of the quantity q_p , will permit to use the experimental metal curves of -1 slope for calculating an α of the order of 10 - 20 kcal/mole and a E_0 of the order of 50 kcal/mole. These figures seem

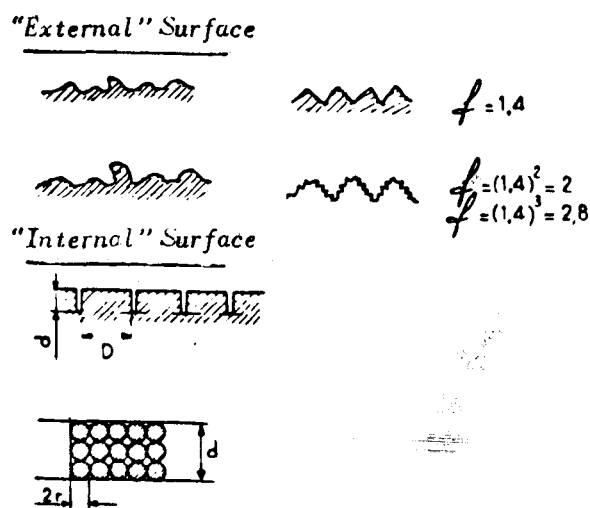


Fig.9 Surfaces

quite reasonable in accordance with our present knowledge on chemisorption (Beeck, Becker, Roberts, etc.; Bibl.13, 14, 15).

A determination of q_p presupposes that it is possible to evaluate the instant at which the physical desorption is terminated and the desorption of the chemisorbed monomolecular layer begins. This distinction is highly schematic but, if the lower limit of the chemisorption is fixed near 5 kcal/mole, a time of the order of 15 - 20 min will be found.

This hypothesis also yields an explanation for the fact that the slope -1 , in log-log coordinates, remains constant up to several hours of pumping because of the fact that n remains relatively high and the condition $\frac{1}{n} \ll \beta$ remains satisfied. Practical experience also shows that, after baking, there is still

a large amount of gas present which escapes as soon as the temperature is increased slightly above the bake-out temperature. An adsorption occurring at atmospheric pressure on the baked walls, if of not too long a duration, will result only in a minor change in the conditions obtained by the baking, and /66 the amount adsorbed at a lower pressure appears quite negligible, which becomes understandable when assuming that, even after baking, n (where $\theta = \frac{n}{n_s}$), remains relatively large and is constituted of particles that are strongly bonded to the solid ($E \sim E_0$).

Several surface models can be imagined (Fig.9).

a) External Surface without Pores or Cracks

In this case, it is difficult to conceive a very large specific surface. In fact, if the roughnesses are compared to square pyramids with a slant height equal to 70% of the base, the value of f will become 1.4. Taking the micro-roughnesses $f = (1.4)^n$ into consideration in the same manner, where n is the number of these superposed pyramids, the maximum conceivable for a macroscopically plane surface apparently will be $n = 4$, i.e., f_{max} will be of the order of 4. The external surface, consequently, cannot be much larger than 4 - 5 times the apparent geometric surface.

b) Internal Surface

The concept "surface" can be extended to a very slight depth below the geometric surface, taking into consideration the internal surface which consists of the total surface of pores and crazings (or of grains) in this layer.

As a practical example, we suggest two models based on this concept:

- 1) A single layer of grains resembling parallelepipeds of $D \times D$ base

dimensions and of a height d , adjoining a specific surface:

$$f = 1 + 4 \frac{d}{D}$$

As an example, for

$d = 10^{-4}$ cm and $D = 10^{-5}$ cm we have $f \sim 40$

$d \backslash D$	10^{-2}	10^{-3}	10^{-4}	10^{-5}
10^{-4}	1.04	1.4	5	40
10^{-3}	1.4	5	40	400

2) Several layers of spherical grains, having a radius of r and a thickness of d :

$$f = \frac{\pi}{2} \cdot \frac{d}{r}$$

As an example, for

$d = 10^{-5}$ cm and $r = 10^{-7}$ cm we have

$d \backslash r$	10^{-4}	10^{-5}	10^{-6}	10^{-7}
10^{-4}	1.6	16	160	1600
10^{-5}	—	1.7	16	160
$5 \cdot 10^{-6}$	—	—	8	80
10^{-6}	—	—	1.6	16

These two latter models thus permit an interior surface several orders of magnitude larger than the apparent geometric surface, over a thickness of the order of 1 micron or even less, depending on the grain dimensions. Obviously, these models must be compared with physical reality, but we will give no 67 fundamental discussion of this aspect of the physics of solid surfaces. It will be recalled here that the Beilby layer which incidentally is highly controversial, assumes the existence, on the polished metal surface, of grains of extremely small dimensions whose surfaces are coated with adsorbed gases. Even

aside from the existence of this almost amorphous layer, the metals conventionally used in vacuum technology are composed of crystallites whose dimensions vary widely according to the treatment used but whose surfaces are coated

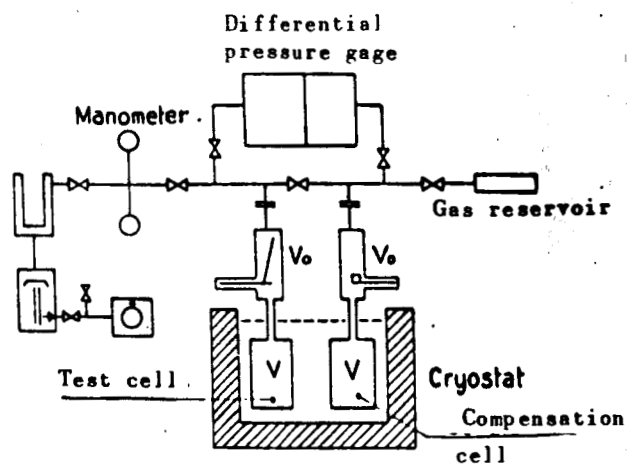


Fig.10 Measurement of a Specific Surface

$$f = \frac{N_L \tau_{\text{gas}} \Delta p}{S_a R 760} \left(\frac{V_0}{T_0} + \frac{V}{T} \right) \left(\frac{p_0}{p} - 1 \right) \left[\frac{1}{C} + \left(1 - \frac{1}{C} \right) \frac{p}{p_0} \right]$$

with impurities and, specifically, with adsorbed gas. Numerous practical experiments have been made (Bibl.13, 14, 15, 16, 17, 18) by the flash-filament technique in which wires or strips of refractory metals such as tungsten or platinum are used; this process uses surfaces consisting of very large grains or even of single crystals, obtained by vacuum-cleanup at very high temperature; thus, it is not surprising that the specific surface in this case is of the order of magnitude of 1.5. Sorption experiments made on thin vapor-deposited films, conversely, have revealed specific surfaces of several orders of magnitude, depending on the degree of fritting of the coating.

In this latter type of experiment, it was proved that an adsorption of gases on this interior surface occurred, by intergranular diffusion. In the case of adsorption, this diffusion may well be the mechanism controlling the

rate of adsorption. Conversely, in the case of desorption which requires a relatively elevated activation energy, the rate of desorption - except during an initial transitory period of operation - is determined by the surface desorption, provided that the layer to be traversed by the particles desorbed from the interior surface is not too thick and that the dimensions of the interstices are very much greater than those of the molecules.

The type of diffusion discussed here and which, in certain cases, may control the entire process should not be confused with diffusion properly speaking, i.e., with intracrystalline diffusion; rather, this type of diffusion is either a surface diffusion due to the mobility of the adsorbed particles or else a Knudsen flow with possibly multiple intergranular adsorptions and desorptions. The mathematical formula complex, for this type of diffusion, is reduced to the same law where q is inversely proportional to the square root of t .

Within the scope of surface studies, we started measuring some specific surfaces by the BET method (Bibl.19, 20), adapted to very thin surfaces by using a differential device which eliminates the influence of the test-chamber surfaces (see schematic sketch in Fig.15).

A differential diaphragm gage is used for measuring the pressure difference produced by the physical adsorption of krypton on specimens transferred from the chamber V_0 at ambient temperature into the chamber V at liquid-nitrogen temperature. A specimen of the same volume but having a much smaller surface is transferred at the same time into the compensation chamber.

The specific surface f can be calculated by

$$f = \frac{N_b \sigma_{Kr} \Delta p}{S_a R 760} \left(\frac{V_0}{T_0} + \frac{V}{T} \right) \left(\frac{p_0}{p} - 1 \right) \left[\frac{1}{C} + \left(1 - \frac{1}{C} \right) \frac{p}{p_0} \right]$$

where

N_L = Loschmidt number

σ_{kr} = surface occupied by one krypton atom

Δp = measured pressure difference

R = ideal gas constant

S_a = apparent geometric surface of the specimen

V_0 = volume of the chamber at the ambient temperature T_0

V = volume of the adsorption chamber at the temperature T

p_0 = vapor pressure of krypton at the temperature T

p = working pressure

C = BET constant: e

(E_1 = binding energy of the first layer
 $f \sim 160$)

E_2 = binding energy of the following layers).

The following preliminary results were obtained for some metals:

aluminum, very thin sheets	$f = 6$
copper, sheets of 1 mm, crude	$f = 14$
stainless steel NS 22 S, sheets of 1 mm, crude ..	$f = 8$
mild steel (silicon steel)	$f = 26$
aluminum, anodized (thickness of layer, 20 μ)	$f = 900$

These figures are of a preliminary nature in that the experimental device did not permit working under the strict conditions required because of the outgassing of the specimens at elevated temperatures in ultrahigh vacuum, the precise measurements of p_0 , and the extremely small pressure differences with respect to the working pressure ($\Delta p/p < 10^{-6}$). Nevertheless, the order of magnitude of the figures obtained for the tested metals agrees well with the order

of magnitude of their desorption rate. However, the values for the specific surfaces are not extremely high, which possibly might indicate that the available experimental device does not yet permit measuring the total surface in view of the fact that the interior surface is partially inaccessible to the krypton atoms, either due to the fact that these atoms are too large for penetrating easily through all the interstices and pores or to the fact that these latter remain partly filled with water vapor which is converted into ice before condensation of the krypton or of other adsorbed gases.

Additional experiments will be run so as to gain better access to the interior surface. /68

9. Desorption of Baked Surfaces

The experimental curves $q = f(t)$ are valid for unbaked surfaces. After bake-out, the rate of desorption normally drops by several orders of magnitude and its measurement becomes quite difficult. Therefore, it is not possible to make any definite statements as to the slope of the curves $q = f(t)$ in this particular case; however, it seems quite possible that the slope will be much more shallow and definitely inferior to 0.5 as soon as rates of the order of 10^7 particles/sec \cdot cm² or less are reached (Bibl.21).

The diffusion of gases from the interior of the matter becomes preponderant and, finally, the permeation of the exterior will establish the lower limit of the desorption rate.

It is of importance to take the influence of adsorption above the residual pressure into consideration. It is certain that the desorption is then no longer independent of the pressure since the number of desorbed particles becomes increasingly a function of the pressure, finally leading to an equili-

brium at a given pressure where just as much gas is adsorbed as desorbed, before the limit established by the permeation is reached so that no more effective desorption can be measured at this particular pressure.

This clearly demonstrates the importance of ultrahigh vacuum techniques for studying very low rates of desorption (of diffusion, or of permeation). Here, measuring the pressures and specifically the very minor pressure differences constitutes an extremely difficult problem. The use of high-sensitivity mass spectrometers becomes indispensable. The influence of the testing devices on the phenomenon to be measured becomes very difficult to eliminate.

One of the most important topics for future research will be an experimental separation of the phenomena of permeation, diffusion, and surface desorption, specifically for very low overall desorption rates.

10. Conclusions

The experimental curves of desorption under vacuum of unbaked metallic materials can be qualitatively and quantitatively explained by the desorption of a monomolecular layer chemisorbed from a surface which, in addition to the external geometric surface, also comprises an interior surface, using extremely simple hypotheses on the binding energies. Several tests and measurements on specific surfaces apparently confirm our interpretation.

We are convinced that our results constitute only a beginning and that the discussion on the subject of desorption is still wide open. For the immediate future, we would suggest the following items for future research:

Specific surface: size, geometry, adequate models for describing the sorption phenomena.

Experimental separation of diffusion and surface desorption phenomena.

Physico-chemical nature of the surface (specifically of oxides).

Binding energies of adsorbate-adsorbent (specifically, H_2O on metallic oxides).

Correlations between these energies, adsorption sites, and rate of deposition.

Mechanisms of dissociation and association of molecules on the surface.

It is obvious that, in many aspects, this research will overlap the research on heterogeneous catalysis (Bibl.19, 22, 23) although the final aims are not always the same and the experimental techniques may often differ.

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